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(71) Applicant (for all designated states except US): STOCKHAUSEN GMBH & CO. KG (DE/DE]: Bäkerpfad 25, 47805 Krefeld (DE).

(72) Inventor; and

(75) Inventor/Applicant (only for US):

PETERSON, Olaf; THEIS, Burkhard; COLBERG, Michael

(74) Agent: WOLFF, Felix.

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(54) Title: METHOD FOR THE PRODUCTION OF AN AQUEOUS ACRYLAMIDE SOLUTION WITH A BIOCATALYST

(57) Abstract: The invention concerns a method and a device for the production of an aqueous acrylamide solution by hydrolysing acrylonitrile in an aqueous solution in the presence of a biocatalyst.

Method for the Production of an Aqueous Acrylamide Solution with a Biocatalyst

The present invention concerns a method and equipment for the production of an aqueous acrylamide solution by hydrolysis of acrylonitrile in an aqueous solution in the presence of a biocatalyst.

The conversion of acrylonitrile to acrylamide in the presence of a suitable biocatalyst in water has been known for may years and is described for example in DE 30 17 005 C2, in which process the biocatalyst is immobilised. In DE 44 80 132 C2 and in EP 0 188 316 B1 special biocatalysts for the conversion of acrylonitrile to acrylamide are described. US 5,334,519 teaches the hydrolysis of acrylonitrile to acrylamide in the presence of biocatalysts and cobalt ions. All these teachings have the disadvantage that the biocatalyst is degraded in the reaction so that its activity is reduced or that unwanted by-products are increasingly produced.

The aim of the present invention is therefore to produce a process in which the biocatalyst is degraded as little as possible during the reaction, the by-products are minimised and the batch time is optimised.

The problem is solved according to the invention by a process for the production of an aqueous acrylamide solution by hydrolysis of acrylonitrile in an aqueous solution in the presence of a biocatalyst, in which the reaction mixture is thoroughly mixed, the reactor has a closed recycling loop through which part of the reaction mixture is pumped and in which there is at least one heat exchanger.

At the start of the reaction, water and the biocatalyst are put into the reactor and brought to a temperature of 15 to 25°C, preferably 16 to 20°C. After the required temperature is reached, the acrylonitrile is dosed into the reactor and the conversion to acrylamide begins. The whole conversion is preferably carried out isothermally. The concentration of the
page 2 biomass in terms of dry substance at the beginning of the reaction is preferably 0.03 - 2.5 g/l, most preferably 0.05 - 1 g/l, and the pH is preferably 6.0 - 8.0, most preferably 6.5 - 7.5.

In the reactor, there is preferably a stirring device with a powerful stirring action, with which the contents of the reactor are mixed homogeneously. In a preferred embodiment cooling coils are fitted to the outside of the reactor so that the reaction mixture can be cooled during the conversion of acrylonitrile to acrylamide.

According to the invention, the reactor is fitted with a closed recycling loop, into which part of the reaction mixture is pumped from the reactor through a closed circuit. In this closed recycling loop there is at least one heat exchanger with which the heat of reaction can be removed The heat exchanger is preferably a tubular heat exchanger in which, to prevent fouling of the heat exchange surfaces, the direction of flow of the reaction mixture is preferably not reversed.

In a preferred embodiment of the present invention the pump and the heat exchanger(s) are arranged to avoid variations of the temperature in the reactor and also to avoid too high an input of energy through the pump. Preferably the pump is a magnetically coupled side canal pump.

Preferably the dosing of the acrylonitrile is into the closed recycling loop, most preferably just before the return of the reaction mixture into the reactor. The dosing is preferably continuous. A frequency controlled piston membrane pump has proved to be especially suitable for dosing the acrylonitrile.

After the end of the acrylonitrile dosing, a post-reaction time of preferably 4 to 20 minutes,

most preferably 5 to 10 minutes, is necessary to allow the acrylonitrile to be converted as completely as possible. During this post-reaction time, it is advantageous for the cooling in the closed loop to be reduced gradually.

3 To optimise the process, the course of the reaction in the reactor is monitored with an in-line measuring device. With this measurement it is possible to control the process very quickly, so that corrections can be made in the event of possible deviations. Preferably the in-line measurement is carried out in the closed recycling loop before the dosing of the acrylonitrile and it is preferred that the acrylonitrile and/or the acrylamide concentration(s) are monitored continuously.

It has been found advantageous to use a Fourier transform infrared (FT-IR) device for the in-line monitoring.

The data from the in-line monitoring can be used to control the conversion. Preferably the amount of acrylonitrile, the rate of flow in the closed recycling loop, the amount in the by-pass and the post-reaction time are controlled.

The process according to the invention can be carried out with any biocatalyst that catalyses the conversion of acrylonitrile to acrylamide. The biocatalyst is however preferably a rhodococcus rhodochrous, which is deposited under the identification number 14230 at the DSMZ, Deutsche Sammlung von Mikroorganismen und Zellkulturen (German Collection of Microorganisms and Cell Cultures) GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Germany.

The process according to the invention has the advantages that the biocatalyst is degraded as little as possible during the conversion of acrylonitrile to acrylamide and hence the amount of the biocatalyst that has to be used is minimised, that fewer by-products are produced, that the conversion of the acrylonitrile goes almost to completion, and that a solution of acrylamide of up to 50% by weight can be produced. The process according to the invention is simple and cost effective to carry out. The reaction times can be reduced drastically with the process of the invention. The optimum use is made of the biocatalyst.

The process according to the invention is preferably carried out in equipment for production of an aqueous acrylamide solution by hydrolysis of acrylonitrile in an aqueous solution in
4 the presence of a biocatalyst with a reactor, a closed recycling loop into which part of the reaction mixture is cycled by a pump, and at least one heat exchanger that is fitted into the closed recycling loop. The equipment is therefore a further object of the current invention.

The reactor is preferably fitted with a stirring device with a powerful stirring action, with which the contents of the reactor are mixed homogeneously. In a preferred embodiment, the outside of the reactor is fitted with cooling coils with which the reaction mixture can be cooled during the conversion of acrylonitrile to acrylamide.

According to the invention, the equipment has a closed recycling loop, into which part of the reaction mixture is pumped from the reactor into a closed circuit. At least one heat exchanger is fitted in this closed recycling loop and is used to remove the heat of reaction. The heat exchanger is preferably a tubular heat exchanger in which, to prevent fouling of the heat exchange surfaces, the direction of the reaction mixture is preferably not changed.

In a preferred embodiment of the present invention, the pump and the heat exchanger(s) are arranged so that both temperature variation in the reactor and too high an input of energy through the pump are avoided. Preferably the pump is a magnetically coupled side canal pump.

Preferably, the acrylonitrile is dosed into the closed recycling loop, most preferably immediately before the return of the reaction mixture into the reactor. The dosing is preferably continuous. A frequency controlled piston-membrane pump has proved to be

especially suitable for dosing the acrylonitrile.

A post-reaction time of preferably 4 to 20 minutes, most preferably 5 to 10 minutes, is necessary after the end of the reaction to convert the acrylonitrile as completely as possible. During this post-reaction period it is advantageous to reduce the cooling gradually.

To optimise the process, the course of the reaction in the reactor is preferably monitored with an in-line measurement. With this measurement, the reaction process can be adjusted very quickly to compensate for any possible variation. Preferably the in-line measurement is carried out in the closed recycling loop before the dosing of the acrylonitrile and it is preferred that the concentrations of the acrylonitrile and/or the acrylamide are measured continuously.

A Fourier transform infrared (FT-IR) device has proved to be advantageous for the in-line measurement.

The results of the measurements can be used to control the process. Preferably the amount of acrylonitrile dosed, the flow rate in the closed recycling loop, the amount in the by-pass and the post-reaction time are controlled.

The process according to the invention has the advantages that the biocatalyst is degraded as little as possible during the conversion of acrylonitrile to acrylamide, and hence the amount of biocatalyst that has to be used is minimised, that fewer by-products are produced, that the conversion of the acrylonitrile is carried out at least almost to completion and that a solution of acrylamide of up to 50% by weight can be produced. The process according to the invention is simple and cost effective to carry out. With the process of the invention, the reaction times can be reduced drastically. The optimum use is made of the biocatalyst.

In the following, the invention will be clarified using Figure 1. This clarification is only as an example and does not limit the overall concept of the invention.

Figure 1 shows a diagram of the process according to the invention or parts or the equipment according to the invention. Before the start of the actual conversion of acrylonitrile to acrylamide, fully deionised water 1 and a suspension 2 that contains the biocatalyst are put into the reactor 3. The contents of the reactor 3 are homogeneously mixed with a mechanical stirrer 16. Cooling coils 17 are fitted to the outside of the reactor 3 and connected to the cold water input 5 and outlet 4. The expert will understand that the contents of the reactor can be pre-warmed to a determined temperature before the actual reaction is begun.

In addition, the reactor 3 has a closed recycling loop 18, through which part of the contents of the reactor can be fed by the magnetically coupled side canal pump 7. In the closed recycling loop 18, there are three tube heat exchangers 6, connected in parallel, with which the contents of the reactor can be heated or cooled. The heat exchangers 6 are also connected in series with the cold water input and outlet. The closed recycling loop has a by-pass line 15, which allows the heat exchangers to be by-passed. The corresponding valves are not shown. The Fourier transform infrared (FT-IR) device 9 for in-line measurement of the concentrations of acrylonitrile and acrylamide in the closed recycling loop 18, and hence in the reactor 3, is also fitted in the closed recycling loop. The sample stream is taken from the closed recycling loop 18 with a piston-membrane pump 8 and pumped continuously into the FT-IR device 9 and analysed there. The measured values are used to control the process. Shortly before the closed recycling loop 18 returns into the reactor 3, the acrylonitrile to be reacted is dosed into it from the acrylonitrile vessel 10 through the membrane dosing pump 11. The vapour zones of the acrylonitrile vessel 10 and the reactor 3 are connected with one another through the swinging pipe 19. The pipe

19 is opened before the dosing of the acrylonitrile starts and is closed again after the dosing is finished. At the end of the reaction, the aqueous acrylamide is separated from the biomass with a ring slit centrifuge 12, and the aqueous acrylamide is collected in the receiver 13 and the biomass in receiver 14.

Patent Claims:

1. A process for production of an aqueous acrylamide solution by hydrolysis of acrylonitrile in an aqueous solution in the presence of a biocatalyst, where the reaction mixture is mixed thoroughly, characterised in that the reactor has a closed recycling loop through which part of the reaction mixture is pumped and into which at least one heat exchanger is fitted.

2. A process according to Claim 1, characterised in that the reactor has cooling, preferably a cooling coil fitted outside the reactor.

3. A process according to Claims 1 or 2, characterised in that the heat exchanger is a tubular heat exchanger in which the reaction mixture is cooled and in which its direction of flow is preferably not changed.

4. A process according to one of Claims 1 to 3, characterised in that the pump and the heat exchanger surfaces are so arranged that sharp variations in the temperature in the reactor and too much energy input through the pump are prevented.

5. A process according to one of Claims 1 to 4, characterised in that the pump is a side canal pump.

6. A process according to one of Claims 1 to 5, characterised in that the acrylonitrile is added into the closed recycling loop, preferably continuously, and most preferably just before the return of the reaction mixture into the reactor.

7. A process according to Claim 7(!), characterised in that the acrylonitrile is dosed with a piston-membrane pump, preferably a frequency controlled piston-membrane pump.

8. A process according to one of Claims 1 to 7, characterised in that the contents of the reactor, consisting of water and biocatalyst, are brought to the temperature of the reaction before the beginning of the reaction.

9. A process according to one of Claims 1 to 8, characterised in that after the acrylonitrile dosing is finished, the cooling is reduced, preferably with a by-pass.

10. A process according to Claim 9, characterised in that the post-reaction time after the end of the acrylonitrile dosing is 4 to 20 minutes, preferably 5 to 10 minutes.

11. A process according to one of Claims 1 to 10, characterised in that the course of the reaction is monitored by in-line measurement.

12. A process according to Claim 11, characterised in that the concentrations of acrylonitrile and/or acrylamide are measured in the closed recycling loop before the point at which the acrylonitrile is dosed.

13. A process according to Claims 11 or 12, characterised in that the measurements are made with an FT-IR device.

14. A process according to one of Claims 11 to 13, characterised in that the in-line measurement is used to control the reaction.

15. A process according to Claim 14, characterised in that the amount of acrylonitrile added, the flow in the closed recycling loop, the by-pass and/or the post-reaction time are controlled.

16. A process according to one of Claims 1 to 15, characterised in that the biocatalyst is a

rhodococcus rhodochrous, which is deposited under the identification number 14230 at the DSMZ, Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Germany.

17. Equipment for the production of an aqueous acrylamide solution by hydrolysis of acrylonitrile in an aqueous solution in the presence of a biocatalyst with a reactor, a closed recycling loop through which part of the reaction mixture is pumped and where at least one heat exchanger fitted in the closed recycling loop.

18. Equipment according to Claim 17 characterised in that the reactor is fitted with cooling, preferably cooling coils fitted outside the reactor.

19. Equipment according to Claims 17 or 18 characterised in that the heat exchanger is a tubular heat exchanger.

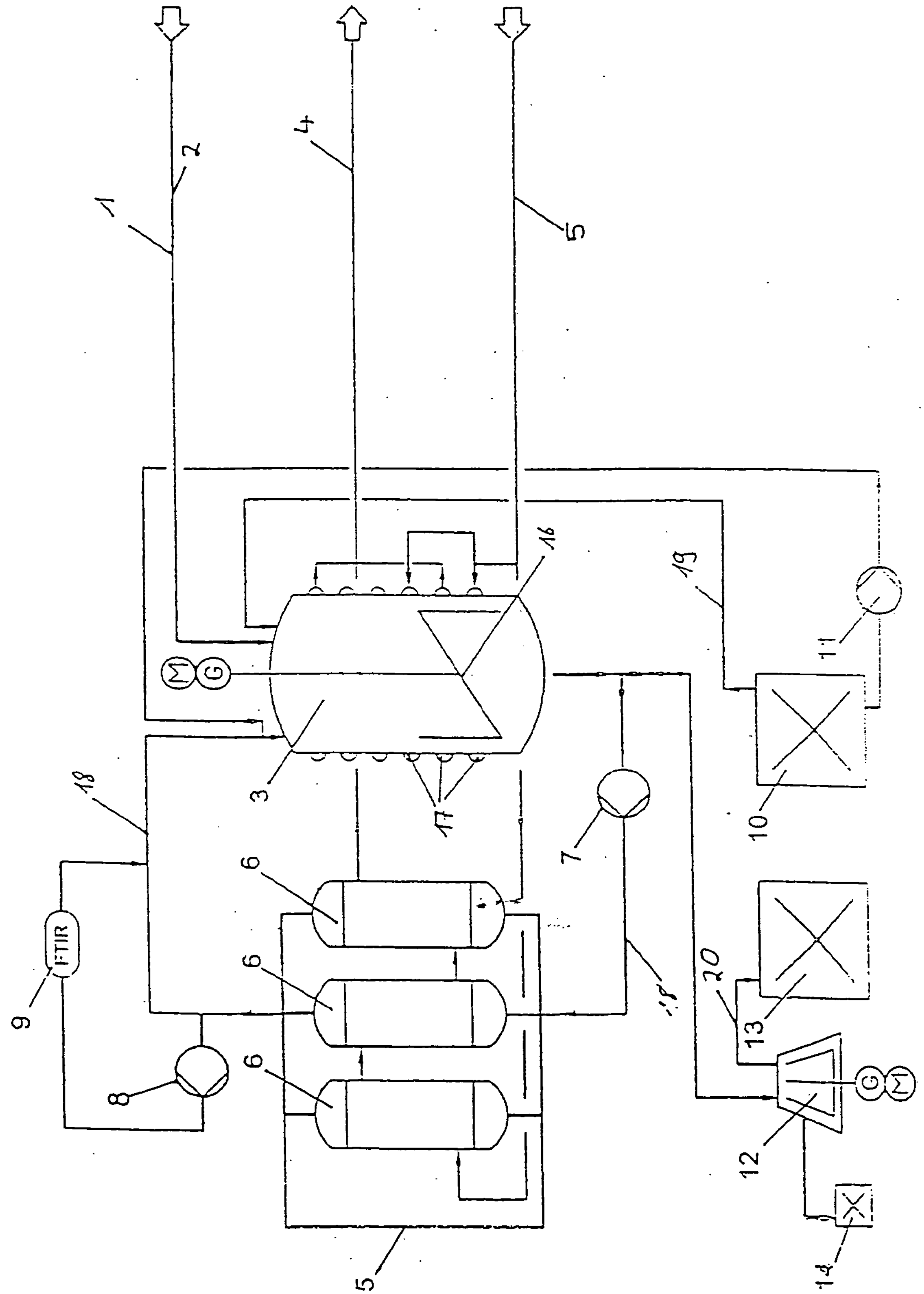
20. Equipment according to one of Claims 17 to 19 characterised in that the pump is a side canal pump.

21. Equipment according to one of Claims 17 to 21 characterised in that an acrylonitrile feed point is fitted in the closed recycling loop, preferably directly before the return of the reaction mixture into the reactor.

22. Equipment according to one of Claims 17 to 21 characterised in that the heat exchanger can be at least partially by-passed.

23. Equipment according to one of Claims 17 to 22 characterised in that an in-line measurement for determining the acrylonitrile and/or acrylamide concentrations is fitted in the closed recycling loop.

24. Equipment according to Claim 23 characterised in that the in-line measurement is made with an FT-IR device.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